Supporting information of "**$(BEDT\text{-}TTF)_3Cu_2(C_2O_4)_3(CH_3OH)_2$: An Organic-Inorganic Hybrid Antiferromagnetic Semiconductor**" by Zhang et al.

Synthesis:

BEDT-TTF was obtained from commercial sources and was used as received without further purification. C_6H_5Cl was dried over $CaCl_2$ and freshly distilled prior to use. CH_3OH was freshly distilled before using.

$(Et_3NH)_2Cu(C_2O_4)_2$ were obtained from methanol solution of $Cu(NO_3)_2{\cdot}2H_2O$, $H_2C_2O_4{\cdot}2H_2O$, and Et_3N.

5.0 mg BEDT-TTF and 30.0 mg $(Et_3NH)_2Cu(C_2O_4)_2$ were dissolved in a mixture of 25.0ml distilled C_6H_5Cl, and 5.0 ml distilled CH_3OH and place in an electrocrystallization cell. The cell was subjected a constant source of 0.10μA for 1 week at room-temperature. Shiny black thin-plat crystals were obtained on the cathode.

Characterization:

The Raman experiment was carried on Renishaw inVia Raman Microscope with λ = 514.5 nm at room temperature (Figure S2).

The polarized IR experiment was performed on the best developed surface of black single crystal on Bio-rad FTS6000/UMA500 Microscope (Figure S3).

A piece of single crystal was selected for X-ray diffraction. Data was collected at 290K and 160 K on Nonius Kappa CCD with Mo Kα (λ=0.71073 Å) radiation. The crystal structure was solved by direct method, hydrogen atoms of ethylene groups were found by calculation, hydrogen atoms of solvent molecules were omitted. All of nonhydrogen atoms were refined anisotropically. The crystallographic data was listed as Table S1.

The dihedral angle between donor molecules, oxalate group and S···S contacts between donor molecules at 290 K and 160 K are listed on Table S2.

The bond-valence calculation of donor molecules at 290 K and 160 K are listed on Table S3.

Magnetization measurement was performed on polycrystalline sample tightly packed in a Al bag on a Quantum Design MPMS 7XL System. Magnetic susceptibility data was corrected for the diamagnetism of the sample by Pascal constant ($-361.715\times10^{-6}cm^3mol^{-1}$) and Al bag.

20 μm gold wires were attached the single crystal by gold paste. The conductivity measurement was performed on the best developed surface of single crystal with four-probe method on a Quantum Design PPMS 9XL system from 2 K to 300 K.

Table S1. Crystallographic data of **1**

Compound	**1**	**1**
formula	C38H32Cu2O14S24	C38H32Cu2O14S24
Fw.	1609.26	1609.26
F(000)	1628	1628
T, K	160	290
crystal system	triclinic	triclinic
space group	$P\ \bar{1}$	$P\ \bar{1}$
a, Å	8.6654(3)	8.7501(3)
b, Å	16.9210(6)	16.9319(6)
c, Å	20.0587(8)	20.1421(7)
α, °	104.959(2)	105.127(1)
β, °	102.301(2)	102.346(2)
γ, °	91.736(2)	91.879(1)
V, Å^3	2761.7(2)	2801.7(2)
Z	2	2
D_c, g/cm^3	1.935	1.907
μ (Mo K_α), mm^{-1}	1.741	1.716
crystal size, mm^3	0.31× 0.28 × 0.02	0.31× 0.28 × 0.02
T_{min} and T_{max}	0.614, 0.963	0.608, 0.960
θ_{min}, θ_{max} , °	0.985, 25.07	0.994, 25.01
no. total reflns.	30239	31941
no. uniq. reflns (R_{int})	9650(0.0696)	9821(0.0660)
no. obs. [I≥2σ(I$_0$)]	5639	4982
no. params	713	713
R1,wR2 [I≥2σ(I$_0$)]	0.0470, 0.0938	0.0464, 0.0881
R1,wR2 (all data)	0.1073,0.1099	0.1257, 0.1049
GOF	0.951	0.914
[a]Δρ, e/Å^3	0.748/-0.715	0.727/-0.566
[b]Max. and mean Δ/σ	0.000/0.000	0.000/0.000
CCDC	836179	836180

Table S2. Bond angles (º) and S···S contacts < 3.65 Å at 160 and 290 K

T, K	160	290
∠ET1-ET2	54.02(2)	54.85(2)
∠ET2-ET3	1.49(4)	1.28(5)
∠ET3-ET1	53.03(2)	53.82(2)
∠Ox1-Ox2	73.64(9)	75.88(9)
∠Ox1-Ox4	64.09(12)	65.15(13)
∠Ox3-Ox2	64.68(12)	64.11(12)
∠Ox3-Ox4	35.79(14)	34.40(15)
∠Ox2-Ox4	79.80(11)	80.23(11)
S···S	3.5195 (0.0016) S2 - S14_$1	3.5909 (0.0017) S2 - S14_$1
	3.4124 (0.0019) S2 - S22	3.4326 (0.0020) S2 - S22
	3.5601 (0.0018) S3 - S14_$5	3.5881 (0.0019) S3 - S14_$5
	3.6052 (0.0017) S3 - S22_$5	3.6470 (0.0018) S3 - S22_$5
	3.4909 (0.0017) S5 - S20_$5	3.5091 (0.0018) S5 - S20_$5
	3.4520 (0.0017) S5 - S24_$5	3.4923 (0.0018) S5 - S24_$5
	3.3859 (0.0017) S6 - S14_$1	3.4365 (0.0018) S6 - S14_$1
	3.4219 (0.0017) S6 - S22	3.4486 (0.0018) S6 - S22
	3.5138 (0.0017) S7 - S14_$5	3.5372 (0.0018) S7 - S14_$5
	3.6530 (0.0018) S7 - S22_$5	3.6924 (0.0019) S7 - S22_$5
	3.6566 (0.0017) S8 - S12_$1	3.6634 (0.0018) S8 - S12_$1
	3.4510 (0.0017) S8 - S16_$1	3.4528 (0.0018) S8 - S16_$1
	3.6316 (0.0018) S8 - S20	3.6493 (0.0020) S8 - S20
	3.4457 (0.0019) S9 - S23_$4	3.4755 (0.0020) S9 - S23_$4
	3.3192 (0.0017) S13 - S23_$4	3.3548 (0.0018) S13 - S23_$4
	3.4698 (0.0019) S15 - S17_$4	3.5032 (0.0019) S15 - S17_$4
	3.4383 (0.0017) S15 - S21_$4	3.4710 (0.0018) S15 - S21_$4

Symmetry Code:

$1 -1+x,y, z; $2 -x,-y,-z; $3 1-x,1-y,-z; $4 2-x,1-y,1-z; $5 1-x,-y,1-z.

ET is abbreviation for BEDT-TTF.

Ox means the oxalate groups in anion as shown in Figure S1. Ox1: O1~O4, C31, C32; Ox2: O5~O8, C33, C34; Ox3: O9, O10, C35; Ox4: O11, O12, C36.

Table S3. Formal Charge of BEDT-TTF (ET) Molecules

$\delta = (b+c)-(a+d)$

$Q = 6.347 - 7.463\delta$

290K

	a	b	c	d	δ	Q
ET1	1.366(5)	1.734(5) 1.734(5) 1.737(4) 1.734(4)	1.756(4) 1.745(4) 1.747(4) 1.746(4)	1.345(6) 1.339(6)	0.776	0.556
ET2	1.371(5)	1.736(5) 1.730(5) 1.728(4) 1.732(5)	1.747(4) 1.746(4) 1.741(4) 1.753(4)	1.345(6) 1.339(6)	0.766	0.630
ET3	1.376(5)	1.729(5) 1.730(5) 1.726(4) 1.736(5)	1.749(4) 1.753(4) 1.744(4) 1.759(4)	1.342(6) 1.339(6)	0.764	0.645
total						1.831

160K

	a	b	c	d	δ	Q
ET1	1.365(6)	1.739(4) 1.738(4) 1.743(4) 1.733(4)	1.752(4) 1.746(4) 1.752(4) 1.745(4)	1.346(6) 1.341(6)	0.781	0.518
ET2	1.364(5)	1.734(5) 1.740(5) 1.733(4) 1.740(5)	1.755(4) 1.751(4) 1.745(4) 1.750(4)	1.346(6) 1.349(6)	0.775	0.563
ET3	1.376(5)	1.735(5) 1.732(4) 1.726(4) 1.744(5)	1.744(4) 1.749(4) 1.746(4) 1.756(4)	1.349(5) 1.339(6)	0.764	0.645
total						1.726

ET1: C1~C10, S1~S8; ET2: C11~C20, S9~S16; ET3: C21~C30, S17~S24 as shown in Figure S1.

Ref:

P. Guionneau, C. J. Kepert, G. Bravic, D. Chasseau, M. R. Truter, M. Kurmoo, P. Day, *Synth. Metal.*, 1997, **86**, 1973.

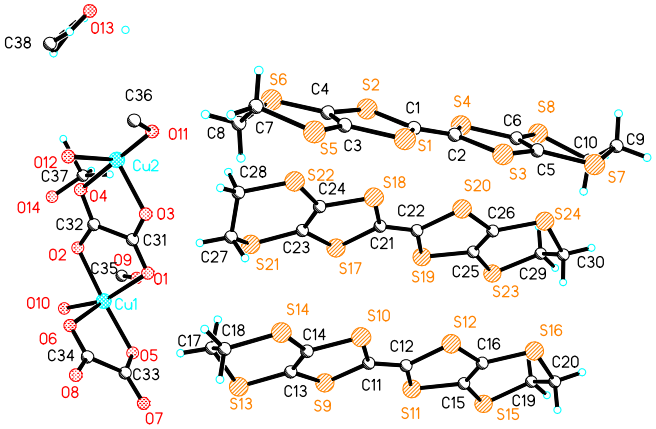

Figure S1. Drawing of **1** in an independent unit.

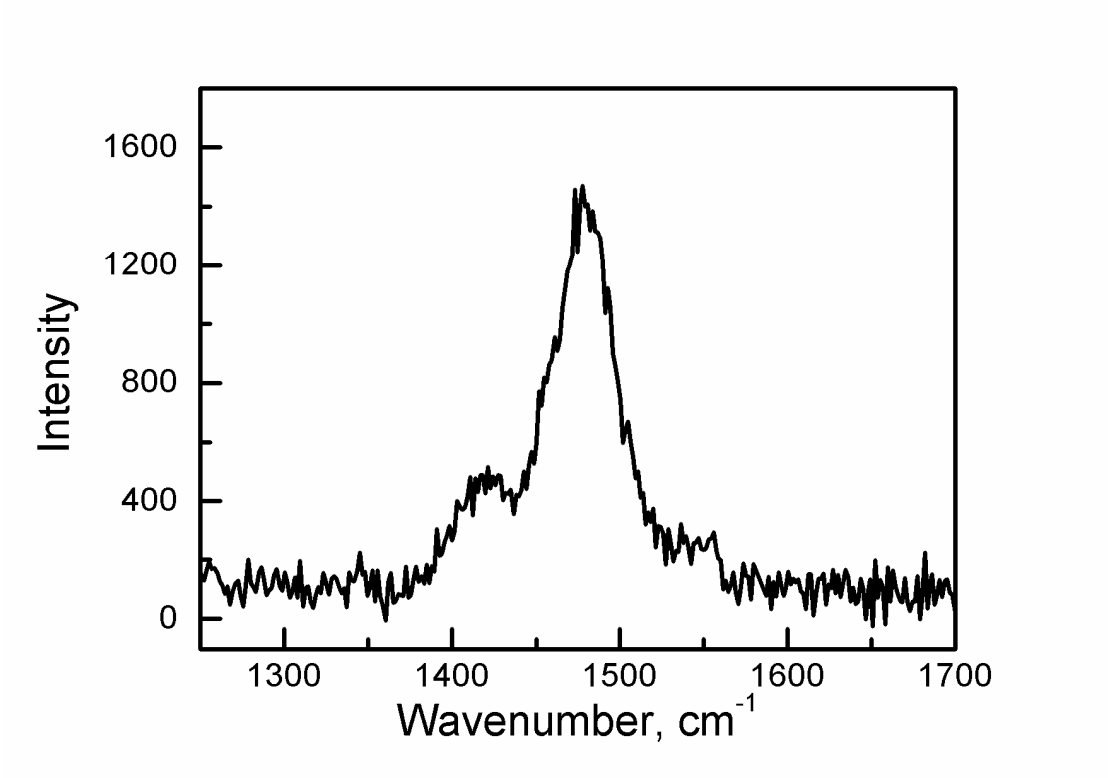

Figure S2. Raman spectra of **1** with λ = 514.5nm at room-temperature.

Ref:
Wang, H. H.; Ferraro, J. R.; Williams, J. M.; Geiser, U.; Schlueter, J. A. *J. Chem. Soc., Chem. Commun.*, 1994, 1893.

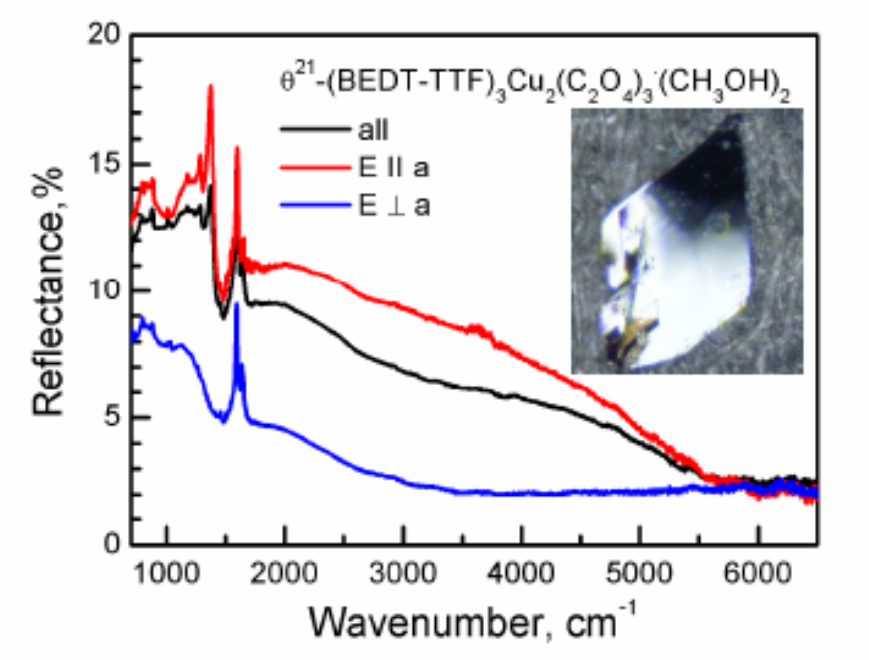

Figure S3. Polarized IR spectrum of **1**.

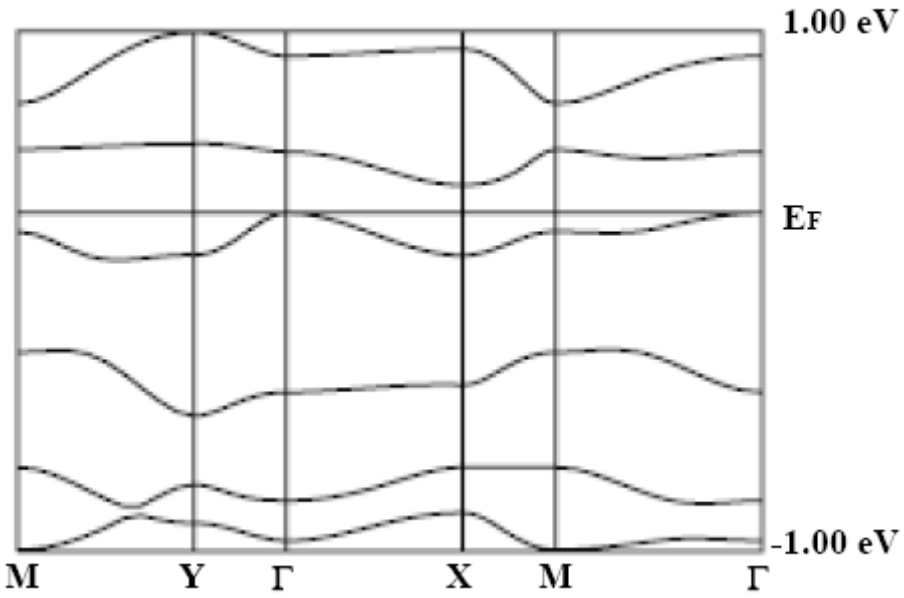

Figure S4. Band structure of **1** at room-temperature.

Ref.:
T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, *Bull. Chem. Soc. Jpn.* 1984, **57**, 627.

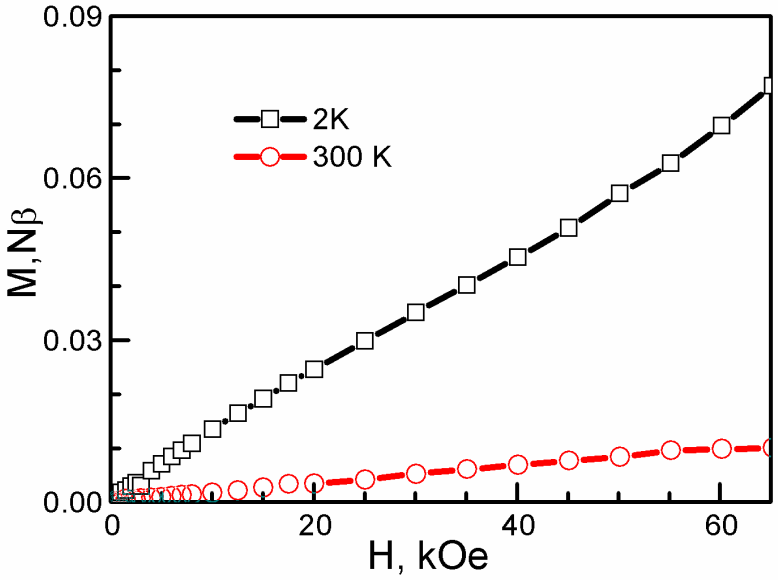

Figure S5. Isothermal magnetization plot for **1** at 2 K and 300 K.